Synopsis

Global warming and depletion in fossil fuels have forced the society to search for alternate, clean sustainable energy sources. An obvious solution to the aforesaid problem lies in electrochemical energy storage systems like fuel cells and batteries. The desirable properties attributed to these devices like quick response, long life cycle, high round trip efficiency, clean source, low maintenance etc. have made them very attractive as energy storage devices. Compared to many advanced battery chemistries like nickel-metal hydride and lithium - ion batteries, metal-air batteries show several advantages like high energy density, ease of operation etc. The notable characteristics of metal - air batteries are the open structure with oxygen gas accessed from ambient air in the cathode compartment. These batteries rely on oxygen reduction and oxygen evolution reactions during discharging and charging processes. The efficiency of these systems is determined by the kinetics of oxygen reduction reaction. Platinum is the most preferred catalyst for many electrochemical reactions. However, high cost and stability issues restrict the use of Pt and hence there is quest for the development of stable, durable and active electrocatalysts for various redox reactions.

The present thesis is directed towards exploring the electrocatalytic aspects of titanium carbonitride. TiCN, a fascinating material, possesses many favorable properties such as extreme hardness, high melting point, good thermal and electrical conductivity. Its metal-like conductivity and extreme corrosion resistance prompted us to use this material for various electrochemical studies. The work function as well as the bonding in the material can be tuned by varying the composition of carbon and nitrogen in the crystal lattice.

The current study explores the versatility of TiCN as electrocatalyst in aqueous and non-aqueous media. One dimensional $TiC_{0.7}N_{0.3}$ nanowires are prepared by simple one step solvothermal method without use of any template and are characterized using various physicochemical techniques. The 1D nanostructures are of several μm size length

and 40 ± 15 nm diameter (figure 1). Orientation followed by attachment of the primary particles results in the growth along a particular plane (figure 2).

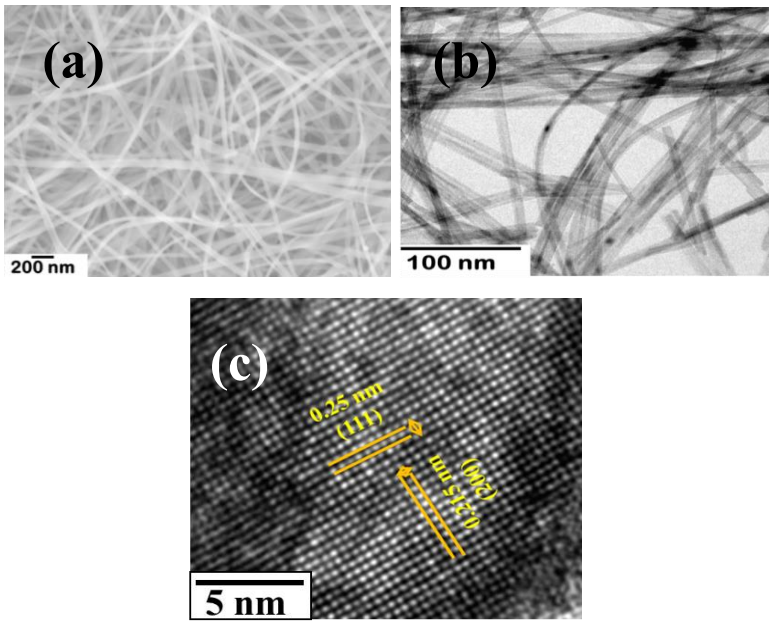

Figure 1. (a) SEM images of $TiC_{0.7}N_{0.3}$ nanowires (b) TEM image and (c) High resolution TEM image showing the lattice fringes.

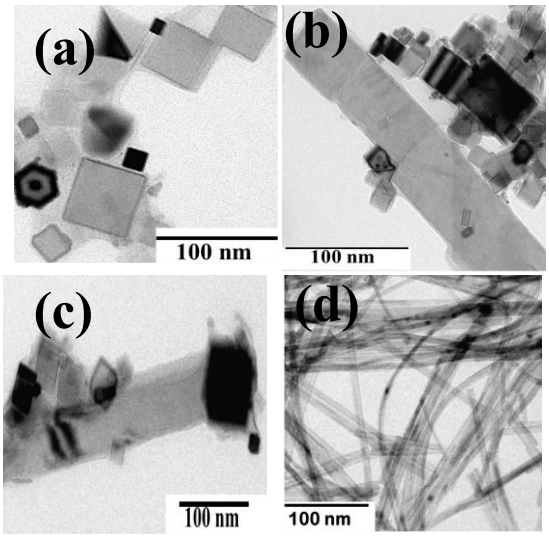

Figure 2. Bright field TEM images obtained at different time scales of reaction. (a) 0 h; (b) 12 h; (c) 72 h and (d) 144 h.

The next aspect of the thesis discusses the electrochemical performance of $TiC_{0.7}N_{0.3}$ especially for oxygen reduction. Electrochemical oxygen reduction reaction (ORR) reveals that the nanowires possess high activity for ORR and involves four electron

process leading to water as the product. The catalyst effectively converts oxygen to water with an efficiency of 85%. A comparison of the activity of different (C/N) compositions of TiCN is shown in figure 3. The composition $TiC_{0.7}N_{0.3}$ shows the maximum activity for the reaction. The catalyst is also very selective for ORR in presence of methanol and thus cross-over issue in fuel cells can be effectively addressed. Density functional theory (DFT) calculations also lead to the same composition as the best for electrocatalysis, supporting the experimental observations.

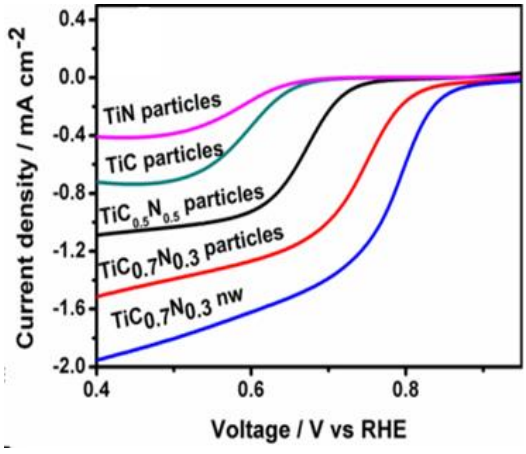

Figure 3. Linear sweep voltammetric curves observed for different compositions of titanium carbonitride towards ORR.

The next chapter deals with the use of $TiC_{0.7}N_{0.3}$ as air cathode for aqueous metal - air batteries. The batteries show remarkable performance in the gel- and in liquid- based electrolytes for zinc - air and magnesium - air batteries. A partial potassium salt of polyacrylic acid (PAAK) is used as the polymer to form a gel electrolyte. The cell is found to perform very well even at very high current densities in the gel electrolyte (figures 4 and 5).

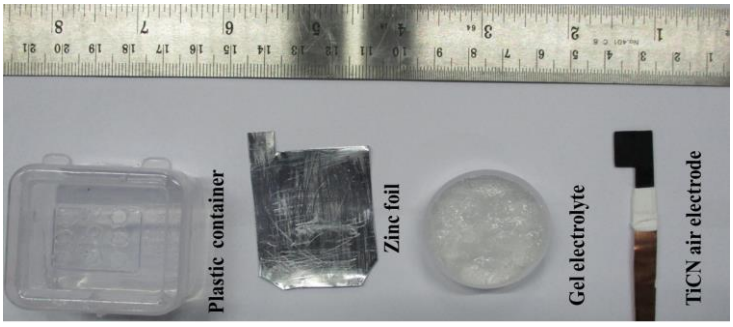

Figure 4 Photographs of different components of the gel - based zinc - air battery.

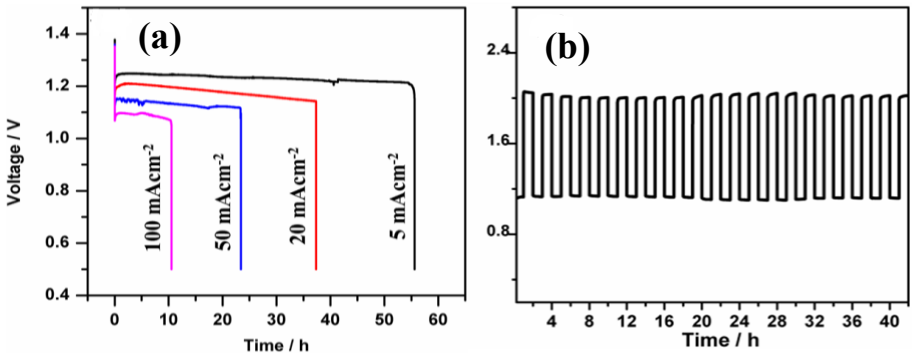

Figure 5. a) Discharge curves at different current densities of 5, 20, 50 and 100 mA/cm^2 for zinc-air system with $TiC_{0.7}N_{0.3}$ cathode b) Charge – discharge cycles at 50 mA/cm^2 for the three electrode configuration with $TiC_{0.7}N_{0.3}$ nanowire for ORR and IrO_2 for OER and Zn electrode (2h. cycle period).

Similarly, the catalytic activity of $TiC_{0.7}N_{0.3}$ has also been explored in non-aqueous electrolyte. The material acts as a bifunctional catalyst for oxygen in non-aqueous medium as well. It shows a stable performance for more than 100 cycles with high reversibility for ORR and OER (figure 6). Li-O_2 battery fabricated with a non-aqueous gel- based electrolyte yields very good output.

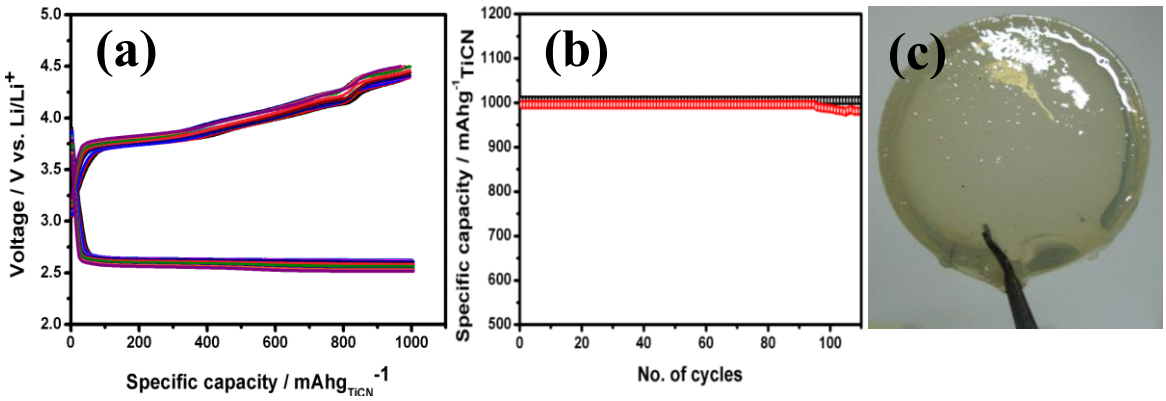

Figure 6. Galvanostatic charge –discharge cycles. (a) at 1 mA/cm^2 (b) specific capacity as a function of no. of cycles (c) photographs of PAN-based gel polymer electrolyte.

Another reaction of interest in non –aqueous medium is $I^-/I_3^{-\cdot}$ redox couple. $TiC_{0.7}N_{0.3}$ nanowires show small peak to peak separation, low charge transfer resistance and hence high activity. The catalyst is used as a counter electrode in dye sensitized a solar cell that shows efficiencies similar to that of Pt, state of the art catalyst (figure 7).

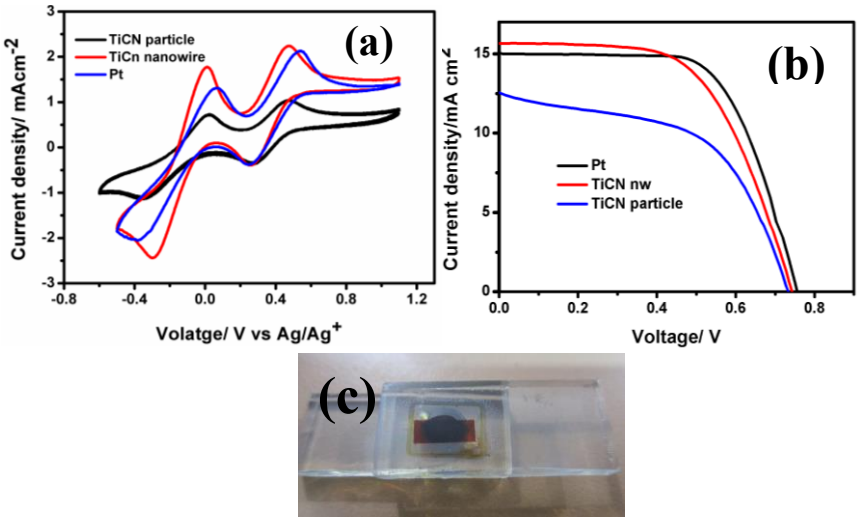

Figure 7 (a) Cyclic voltammograms for I^-/I_3^- redox species on $TiC_{0.7}N_{0.3}$ nanowires (red), $TiC_{0.7}N_{0.3}$ particle (black) and Pt (blue). (b) Photocurrent density - voltage characteristics for DSSCs with different counter electrodes. $TiC_{0.7}N_{0.3}$ nanowire (black), $TiC_{0.7}N_{0.3}$ particle (blue), Pt (red). (c) Photograph of a sample cell.

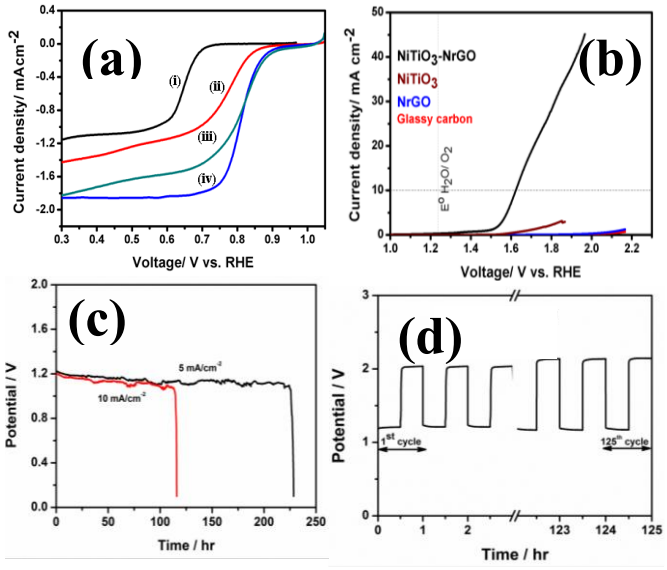

Figure 8 a) Comparison ORR activity for (i) $NiTiO_3$(black), (ii) N-rGO (red), (iii) $NiTiO_3$ – N-rGO (green) and (iv) Pt/C (blue) (b) Linear sweep voltammograms for OER observed on $NiTiO_3$ – N-rGO composite (black), $NiTiO_3$ (brown), N-rGO (blue), glassy carbon (red) in 0.5 M KOH. (c) Galvanostatic discharge curves of $NiTiO_3$ – N-rGO as air electrode (d) Charge – discharge cycle at 5 mA/cm^2 for the rechargeable battery with 10 min. cycle period.

The last part of the thesis discusses about a ceramic oxide, nickel titanate. The electrocatalytic studies of the material towards ORR and OER reveal that the catalyst shows remarkable performance as a bifunctional electrode. A gel - based zinc - air battery fabricated with nickel titanate – reduced graphene oxide composite shows exceptional performance of 1000 charge-discharge cycles in the rechargeable mode (figure 8). Of course, the primary battery configuration works very well too

The thesis contains seven chapters on the aspects mentioned above with summary and future perspectives given as the last chapter. An appendix based on TiN nanotubes and supercapacitor studies is given at the end.